

0.8,<sup>1</sup> from which one infers  $k_2/k_{-1} \approx 0.4$ . Thus  $\gamma(0) \approx 0.04k_1$ , which means that at zero field about one collision in 25 leads to annihilation.

The high-field anisotropy measurements represent a kind of zero-frequency magnetic resonance spectroscopy by virtue of the occurrence of the pair level-crossing resonances. The positions of these resonances can yield information concerning the zero-field splitting parameters and the orientation of the dipolar tensor while the line shapes depend on the nature and strength of the intertriplet interaction. In addition to the high-field-pair level crossings, the theory also leads one to expect single-particle level-crossing resonances when the field is oriented along a principal axis of the dipolar tensor and the strength is such that the Zeeman and zero-field splittings are about equal. Such resonances have indeed been found at the expected positions in low-field anisotropy measurements in anthracene.<sup>4</sup>

The theory presented here can not be regarded as confirmed until detailed calculations of field dependence and line shapes have been carried out and compared with experiment. Such calculations are currently underway. However, even at this stage it is clear that magnetic-field experiments provide a powerful tool for elucidating the details of the triplet-triplet annihilation process and for studying the spin states of triplet excitons.

\* Contribution No. 1431.

<sup>1</sup> R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippen, *Phys. Rev. Letters* **19**, 285 (1967).

<sup>2</sup> H. Sternlicht and H. M. McConnell, *J. Chem. Phys.* **35**, 1793 (1961).

<sup>3</sup> J. H. van der Waals and M. S. de Groot, *Mol. Phys.* **2**, 333 (1959).

<sup>4</sup> R. C. Johnson and R. E. Merrifield (unpublished).

## Energy Dependence of Energy Partition in Products of Direct Reactions: Crossed-Beam Studies and a New Model

P. HIERL, Z. HERMAN,\* J. KERSTETTER, AND R. WOLFGANG

*Department of Chemistry, Yale University, New Haven, Connecticut*  
and *Department of Chemistry, University of Colorado,*  
*Boulder, Colorado*

(Received 24 July 1967)

In a recent Communication,<sup>1</sup> we described first experiments with a crossed-beam apparatus (EVA) operating in the "hot" energy range 0.1–25 eV. It was found that a simple ion-molecule reaction,  $N_2^+ + D_2 \rightarrow N_2D^+ + D$ , did not involve an intermediate long-lived complex. A new model of direct reaction taking into account long-range polarization forces was described and found to provide a good representation of results obtained.<sup>1,2</sup>

We now report findings on the distribution of the reaction energy between internal and translational

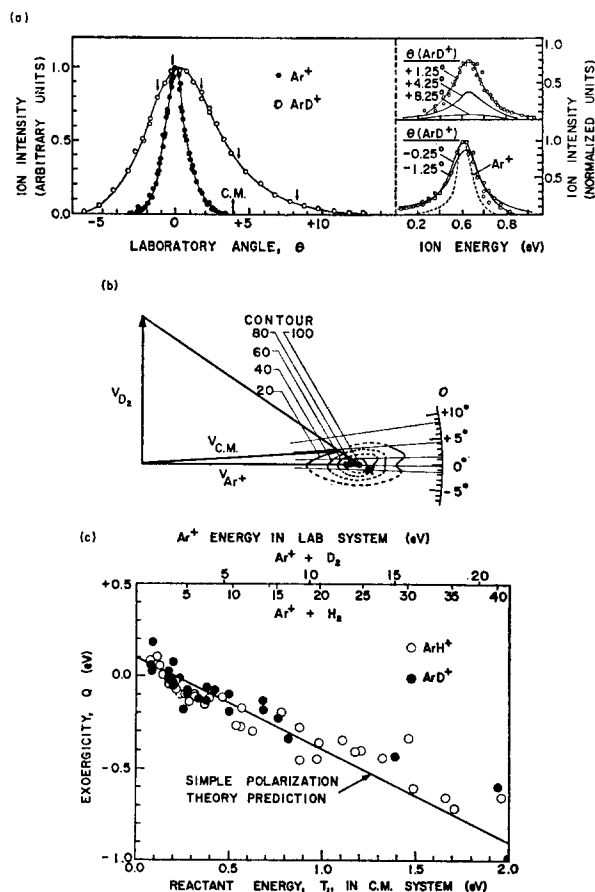


FIG. 1. (a) Angular distribution (left) and energy spectra (right) taken at angles indicated by arrows for  $ArD^+$  produced by crossing of 0.61 eV  $Ar^+$  with thermal (55°C)  $D_2$  molecular beam. (b) Newton diagram<sup>2</sup> of above data. Intensity contours are given in LAB system.  $\times$  indicates position of maximum intensity after transformation to center-of-mass system (see Ref. 2). (c) Dependence of translational exoergicity  $Q$  upon reactant collision energy  $T_1$ . Plot is for maximum intensity in LAB system. (If position of maximum intensity in c.m. system were plotted, a somewhat higher intercept  $Q_0$  would result.)

modes of the products, and on the dependence of this on initial kinetic energy. Results on the systems  $Ar^+ + D_2 \rightarrow ArD^+ + D$ , and  $Ar^+ + H_2 \rightarrow ArH^+ + H$  are presented here.<sup>3</sup> They provide a test for the new model of direct reaction.

The experimental technique, involving crossed beams of monoenergetic  $Ar^+$  and thermal hydrogen, has been described.<sup>1,2</sup> Typical results on the angular distribution and energy spectrum of  $ArD^+$  at 0.61 eV LAB (0.08 eV c.m.) are shown in Fig. 1. They are summarized as intensity contours<sup>4</sup> on the appropriate Newton diagram. As in the case of  $N_2^+$  reaction with  $D_2$ ,<sup>1</sup> the data are inconsistent with a symmetrical distribution around the center of mass, which is required if an intermediate complex having a lifetime of more than a few rotational periods is formed. Furthermore, the spectator stripping model is also inadequate.<sup>1</sup>

From the data, the translational exoergicity of the reaction may be computed. This quantity is defined as the net conversion of internal to translational energy:  $Q = T_4 - T_1$ , where  $T_4$  is the kinetic energy of the products and  $T_1$  that of the reactants (both in the center-of-mass system).  $T_1$  is known from the initial conditions and  $T_4$  is computed from the measured velocity of  $\text{ArD}^+(\text{ArH}^+)$  at the peak in the angular and velocity distributions. Values of  $Q$  thus determined for the position of maximum intensity<sup>4</sup> are shown in Fig. 1. The remarkable conclusion emerges that the translational exoergicity is not only highly energy dependent, but changes sign: at low reactant velocities there is a net conversion of internal to translational energy of products, while at higher velocities an increasing portion of the kinetic energy of the reactants appears as internal energy of products.

According to the simple polarization theory postulated earlier, the approaching reactants are accelerated towards each other by the ion-induced-dipole force between them. After atom transfer occurs, the products are similarly decelerated. Using this model, it can readily be shown<sup>2</sup> that for a relatively heavy ion reacting with homonuclear hydrogen the translational exoergicity is  $Q \approx \frac{1}{2}P - P' - \frac{1}{2}T_1$ .  $P$  and  $P'$  are ion-induced-dipole energies of the reactant and product pairs, respectively (having the form  $\alpha e^2/2r_c^4$ , where  $\alpha$  is the appropriate polarizability and  $r_c$  the distance of closest approach). The single<sup>5</sup> adjustable parameter  $r_c$  is fitted for the lowest energy. It corresponds to a closest  $\text{Ar}^+-\text{D}$  distance of about  $1.44 \pm 0.15 \text{ \AA}$ .<sup>6</sup> (This agrees reasonably well with the known bond distance of  $1.27 \text{ \AA}$  for the isoelectronic molecule  $\text{DCl}$ .)

Predictions of this model as to  $Q$  at all energies are shown as the solid line in Fig. 1. The agreement of theory and experiment for both isotopic systems supports the proposed mechanism and indicates that long-range forces dominate the dynamics of these direct reactions.

This work was supported by the U.S. Atomic Energy Commission and the National Aeronautics and Space Administration. We greatly appreciate the help of Alfred Lee in all phases of this work.

\* Present address: Institute of Physical Chemistry, Czechoslovak Academy of Science, Prague, Czechoslovakia.

<sup>1</sup> Z. Herman, J. D. Kerstetter, T. L. Rose, and R. Wolfgang, *J. Chem. Phys.* **46**, 2844 (1967).

<sup>2</sup> For a fuller description of the experiment and the mathematical elaboration of the model, see Z. Herman, J. Kerstetter, T. Rose, and R. Wolfgang, *Discussions Faraday Soc.* **44**, 123 (1967).

<sup>3</sup> R. D. Fink and J. S. King, Jr., *J. Chem. Phys.* **47**, 1857 (1967); L. D. Doverspike, R. L. Champion, and T. L. Bailey, *ibid.* **45**, 4385 (1966); and A. Ding, K. Lacmann, and A. Henglein, *Ber. Bunsenges. Physik. Chem.* **71**, 596 (1967), have independently measured product velocities for the same reactions. However, their work did not extend to the critical very low energy range and furthermore involved a static target (with a three-dimensional distribution of target velocities) rather than a crossed beam. Nevertheless, their data accords with our model, although the magnitude of the apparent effect as found by Fink and Henglein is larger.

<sup>4</sup> Intensities on the Newton diagram are given relative to the laboratory system. Values of  $Q$  given here correspond to the position of maximum intensity in the laboratory system (see Ref. 2, Footnotes 14, 16, and 21).

<sup>5</sup> There are actually two such parameters  $r_c$ , corresponding to the closest approach of the reactants,  $\text{Ar}^+-\text{H}_2$ , and closest approach of products  $\text{ArH}^+-\text{H}$ . However, they are related by half the H-H bond distance.

<sup>6</sup> The uncertainty quoted is based on our estimated uncertainty in the intercept of  $Q$  at 0 eV. A transformation of the Newton diagram to the c.m. is difficult,<sup>4</sup> but would result in a larger  $Q(0 \text{ eV})$  and an  $\text{Ar}-\text{D}^+$  distance which would be smaller by  $\sim 0.3 \text{ \AA}$  (see Ref. 2, Footnote 21).

## Mercury 2537-Å Emission as a Test for $\text{N}_2(A \ ^3\Sigma_u^+)$ in Active Nitrogen\*

D. H. STEDMAN, J. A. MEYER, AND D. W. SETSER†

Chemistry Department, Kansas State University  
Manhattan, Kansas

(Received 22 January 1968)

The main chemically reactive component of active nitrogen is ground-state N atoms.<sup>1</sup> Nevertheless, metastable  $\text{N}_2$  molecules,<sup>2</sup> highly vibrationally excited ground-state  $\text{N}_2$ ,<sup>3</sup> and electronically excited nitrogen atoms<sup>4,2a</sup> have also been directly observed or invoked to explain some reactions of active nitrogen. Dugan<sup>5</sup> has offered striking evidence for a metastable species in active nitrogen, apparently  $\text{N}_2(A \ ^3\Sigma_u^+)$ , whose concentration was first order in  $[\text{N}]$ . Recently Thrush<sup>6a</sup> reinterpreted the Vegard-Kaplan (A-X) emission data obtained by Noxon<sup>6b</sup> showing that the emission intensity was first order in  $[\text{N}]$  and in  $[\text{N}_2]$ . We will present data which, combined with these results, show that  $\text{Hg}(^3P_1 \rightarrow ^1S_0)$  emission at 2537 Å can be used to measure relative  $[\text{N}_2(A \ ^3\Sigma_u^+)]$  in active nitrogen. The excitation of Hg 2537-Å emission by  $\text{N}_2(A)$  was first demonstrated by Brennen and Kistiakowsky<sup>7</sup> and has since been employed in more complicated systems<sup>8</sup> as supporting evidence for the presence of  $\text{N}_2(A \ ^3\Sigma_u^+)$ . However, the data shown here are the first direct kinetic analysis of the excitation processes.

Nitrogen atoms were generated by a microwave discharge through pure  $\text{N}_2$  or  $\text{N}_2/\text{Ar}$  mixtures in an ordinary discharge flow apparatus. Values of  $[\text{N}]$  were determined by NO titration. Mercury vapor was added to the flow stream with a metered flow of nitrogen or argon which had been saturated with mercury at room temperature. Figure 1 shows that the intensity ( $I$ ) is first order in  $[\text{N}]$ , and it was also shown to be first order in  $[\text{Hg}]$  and total pressure, with  $\text{N}_2$  or Ar carrier gas.  $I$  was independent of both time after the discharge and contact time with the Hg. This shows that the exciting species is being continuously generated in active  $\text{N}_2$ .

The simplest explanation of the observations is the